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(57) Abstract

Disclosed are anti-dandruff shampoo compositions which comprise: (a) from about 7 % to about 30 % by weight of a detersive surfactant selected form the group consisting of anionic surfactant, amphoteric surfactant, and mixtures thereof; (b) from about 0.1 % to about 10 % by weight of an antimicrobial agent; (c) from about 0.5 % to about 10 % by weight of a suspending agent; (d) from about 0.01 % to about 1.0 % by weight of a cationic guar polymer having a charge density of from about 0.1 to about 3meq/gm; (e) a cool-feeling agent selected from the group consisting of borneol, camphor, cineol menthane, glycosil-mono-mentyl-oacetate, menthol, 3-1-menthoxypropane-1-2-diol, menthyl malonate, 1-menthyl-3-hydroxybutyrate, menthyl salicylate, peppermint, spearmint, and mixtures thereof; and (f) from about 40 % to about 92 % by weight of water; wherein at least about 50 % by weight of the cationic guar polymer is in coacervate form, said coacervate comprising detersive surfactant and cationic guar polymer.

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ANTI-DANDRUFF SHAMPOO COMPOSITION COMPRISING A COOL-FEELING AGENT

BACKGROUND

Various anti-dandruff shampoo compositions are commercially available or otherwise known in the shampoo art. These compositions typically include particulate, crystalline antimicrobial agents dispersed and suspended throughout the composition. Antimicrobial agents used for this purpose include sulfur, selenium sulfide and heavy metal salts of pyridinethione. During the shampooing process, these antimicrobial agents deposit on the scalp to provide anti-dandruff activity.

Many anti-dandruff shampoos, however, do not provide sufficient antimicrobial agent deposition during the shampooing process. Without such deposition, the antimicrobial agents simply rinse away during shampooing and therefore provide little or no anti-dandruff activity. In addition, the detersive surfactants in these shampoo compositions which are designed to remove oil, grease, dirt, and particulate matter will also carry away particulate antimicrobial agents during rinsing, thus further decreasing deposition and anti-dandruff activity.

Deposition of particulate antimicrobial agents is especially difficult in anti-dandruff shampoo compositions containing crystalline suspending agents. These suspending agents help disperse and suspend particulate antimicrobial agents in the shampoo composition. These suspending agents, however, adversely affect lathering performance. It has therefore become conventional practice to enhance the lathering performance of these shampoos by increasing detersive surfactant concentrations or by adding foam boosters, both of which further decrease deposition of particulate antimicrobial agents from the shampoo compositions.

Additionally, some consumers have come to expect and/or desire a refreshing sensation to be imparted to the scalp during and/or after shampooing. Unfortunately previously known shampoo compositions do not provide sufficient

deposition of materials useful for imparting such a refreshing sensation. Furthermore, such refreshing materials tend not to have an optimum shelf stability in previously known shampoo compositions.

Based on the foregoing, there is a need for an anti-dandruff shampoo composition having improved deposition of antimicrobial agents (particularly particulate antimicrobial agents) as well as improved deposition of agents which impart a refreshing feeling to the scalp.

SUMMARY

The present invention is directed to anti-dandruff shampoo compositions which comprise: (a) from about 7% to about 30% by weight of a detersive surfactant selected from the group consisting of anionic surfactant, amphoteric surfactant, and mixtures thereof; (b) from about 0.1% to about 10% by weight of an antimicrobial agent; (c) from about 0.5% to about 10% by weight of a suspending agent; (d) from about 0.01% to about 1.0% by weight of a cationic guar polymer having a charge density of from about 0.1 to about 3meq/gm; (e) a cool-feeling agent selected from the group consisting of borneol, camphor, cineol menthane, glycosil-mono-mentyl-oacetate, menthol, 3-1-menthoxypropane-1-2-diol, menthyl malonate, 1-menthyl-3-hydroxybutyrate, menthyl salicylate, peppermint, spearmint, and mixtures thereof; and (f) from about 40% to about 92% by weight of water; wherein at least about 50% by weight of the cationic guar polymer is in coacervate form, said coacervate comprising detersive surfactant and cationic guar polymer.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION

While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

Herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All percentages, parts and ratios are based upon the total weight of the shampoo compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials.

The aspects and embodiments of the present invention set forth in this document have many advantages. For example, it has now been found that in certain embodiments of the present invention, the select cationic deposition polymers are especially effective in providing enhanced deposition of antimicrobial agents, especially particulate antimicrobial agents, from a shampoo composition. The select polymers are cationic derivatives of guar gum which have been found to be most effective when used in combination with crystalline suspending agents and high levels of anionic, amphoteric or zwitterionic surfactant in an anti-dandruff shampoo composition.

Additionally, it has been found in certain embodiments of the present invention that the incorporation of cool-feeling agents in a shampoo composition comprising such select cationic deposition polymers provides improved deposition of the cool-feeling agents to the scalp.

Certain embodiments may also provide improved shelf stability. Without being bound by theory, it is believed the large size of the cationic guar polymer component improves phase stability of a shampoo comprising the cool-feeling agent.

Certain embodiments provide anti-dandruff treatment, as well as impart a cool-feeling sensation to the scalp of the user.

Certain embodiments may provide high lathering in combination with improved deposition and/or improved stability of the cool-feeling agents.

A. <u>Detersive Surfactant</u>

The shampoo compositions of the present invention include a detersive surfactant selected from the group consisting of anionic surfactants, amphoteric surfactants, and combinations thereof. The shampoo compositions preferably include an anionic surfactant. The detersive surfactant provides the shampoo compositions with cleaning performance.

1. <u>Anionic surfactant</u>

The detersive surfactant component of the shampoo compositions is preferably an anionic surfactant. Concentrations of anionic surfactant can range

from about 7% to about 30%, preferably from about 10% to about 25%, more preferably from about 12% to about 22%, by weight of the shampoo compositions.

Anionic surfactants useful herein include alkyl and alkyl ether sulfates. These materials have the respective formulae $ROSO_3M$ and $RO(C_2H_4O)_xSO_3M$, wherein R is alkyl or alkenyl of from about 8 to about 30 carbon atoms, x is 1 to about 10, and M is hydrogen or a cation such as ammonium, alkanolammonium (*e.g.*, triethanolammonium), a monovalent metal cation (*e.g.*, sodium and potassium), or a polyvalent metal cation (*e.g.*, magnesium and calcium). Preferably, M should be chosen such that the anionic surfactant component is water soluble. The anionic surfactant or surfactants should be chosen such that the Krafft temperature is about 15°C or less, preferably about 10°C or less, and more preferably about 0°C or less. It is also preferred that the anionic surfactant be soluble in the composition hereof.

Krafft temperature refers to the point at which solubility of an ionic surfactant becomes determined by crystal lattice energy and heat of hydration, and corresponds to a point at which solubility undergoes a sharp, discontinuous increase with increasing temperature. Each type of surfactant will have its own characteristic Krafft temperature. Krafft temperature for ionic surfactants is, in general, well known and understood in the art. See, for example, Myers, Drew, Surfactant Science and Technology, pp. 82-85, VCH Publishers, Inc. (New York, New York, USA), 1988 (ISBN 0-89573-399-0).

In the alkyl and alkyl ether sulfates described above, preferably R has from about 12 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be derived from fats, *e.g.*, coconut oil, palm oil, tallow, or the like, or the alcohols can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil and palm oil are preferred herein. Such alcohols are reacted with 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates which can be used in the present invention are sodium and ammonium salts of coconut alkyl triethylene glycol

ether sulfate; tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from 1 to about 4 moles of ethylene oxide. Such a mixture also comprises from 0% to about 20% by weight C_{12-13} compounds; from about 60% to about 100% by weight of C_{14-16} compounds, from 0% to about 20% by weight of C_{17-19} compounds; from about 3% to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45% to about 90% by weight of compounds having a degree of ethoxylation of from 1 to about 4; from about 10% to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1% to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

Other suitable anionic surfactants are the water-soluble salts of organic, sulfuric acid reaction products of the general formula $[R^1\text{-}SO_3\text{-}M]$ where R^1 is selected from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is as previously described above in this section. Examples of such surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, *e.g.*, SO_3, H_2SO_4, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{10-18} n-paraffins.

Other anionic surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2, etc., when used in the gaseous form. The α-olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably

about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process. A specific α-olefin sulfonate mixture of the above type is described more fully in U.S. Patent 3,332,880, to Pflaumer and Kessler, issued July 25, 1967.

Still other suitable anionic surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut or palm oil; or sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other similar anionic surfactants are described in U.S. Patents 2,486,921, 2,486,922, and 2,396,278.

Another class of anionic surfactants suitable for use in the shampoo compositions are the β-alkyloxy alkane sulfonates. These compounds have the following formula:

$$R^1\!-\!\underset{}{\overset{\displaystyle OR^2}{\overset{|}{C}}}H\!-\!CH_2\!-\!SO_3M$$

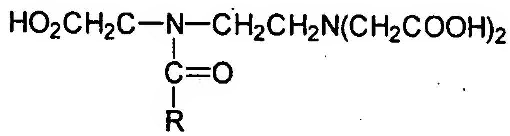
where R^1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R^2 is a lower alkyl group having from about 1, preferred, to about 3 carbon atoms, and M is as hereinbefore described. Many other anionic surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and in U.S. Patent 3,929,678.

Another class of suitable anionic surfactants are amino acid surfactants which are surfactants that have the basic chemical structure of an amino acid compound, *i.e.*, that contains a structural component of one of the naturally-occurring amino acids.

Also useful herein are N-acyl-L-glutamates such as N-cocoyl-L-glutamate and, N-lauroyl-L-glutamate, sodium lauryl aminodiacetic acid, laurimino diproprionate, and N-lauryl-β-imino-dipropionate, N-acyl-L-aspartate, polyoxyethylene laurylsulfosuccinate, disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetra sodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; the diamyl ester of sodium

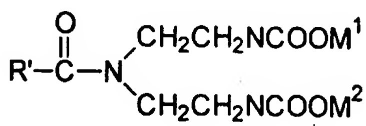
sulfosuccinic acid; the dihexyl ester of sodium sulfosuccinic acid; and the dioctyl ester of sodium sulfosuccinic acid, and 2-cocoalkyl N-carboxyethyl N-carboxyethoxyethyl imidazolinium betaine.

Other suitable anionic surfactants include those of the following formula (I) and (II):



(I)

wherein R is an alkyl of 12 to 18 carbons; and



(II)

wherein R' is a straight or branched alkyl or alkenyl of 5 to 21 carbons; and M^1 and M^2, independently, are hydrogen, alkaline metal, alkaline earth metal, ammonium, alkyl or alkenyl ammonium of 1 to 22 carbons, alkyl or alkenyl substituted pyridinium of 1 to 18 carbons, or basic amino acids. Suitable examples of formula (I) include acid salts of N-acyl-N,N'-ethylenediaminetriacetic acid, such as sodium, triethanolamine and ammonium salts of lauroyl-N,N'-ethylenediaminetriacetic acid, myristoyl-N,N'-ethylenediaminetriacetic acid, cocoyl-N,N'-ethylenediaminetriacetic acid, and oleoyl-N,N'-ethylenediaminetriacetic acid. Suitable examples of formula (II) include acid and salt forms of N-hexanoyl-N-carboxyethyl-β-alanine, N-octanoyl-N-carboxyethyl-β-alanine, N-decanoyl-N-carboxyethyl-β-alanine, N-lauroyl-N-carboxyethyl-β-alanine, N-tetradecanoyl-N-hydroxyethyl-β-alanine, N-hexadecanoyl-N-carboxyethyl-β-alanine, N-isostearoyl-N-carboxyethyl-β-alanine, and N-oleoyl-N-carboxyethyl-β-alanine.

Preferred anionic surfactants for use in the shampoo compositions include ammonium laureth sulfate, triethylamine laureth sulfate, triethanolamine laureth sulfate, monoethanolamine laureth sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium laureth sulfate, potassium laureth sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, N-cocoylalaninate, N-acyl-N-methyl-β-alaninate, sodium laurylsarcosinate, cocoyl sarcosine, lauroyl taurate, lauroyl lactylate, N-acyl potassium glysine,

lauroamphohydroxy propylsulfonate, cocoglyceride sulfate, lauroyl isethionate, lauroamphoacetate, and mixtures thereof.

2. Amphoteric Surfactants

Amphoteric surfactants useful herein include those called zwitterionic surfactants in the art. Amphoteric surfactants useful herein include the derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical is straight or branched and one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, *e.g.*, carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Amphoteric surfactants for use herein include the derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals are straight or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group, *e.g.*, carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:

$$\begin{array}{c} \qquad (R^3)_x \\ \qquad | \\ R^2-\overset{+}{Y}-CH_2-R^4-Z \end{array}$$

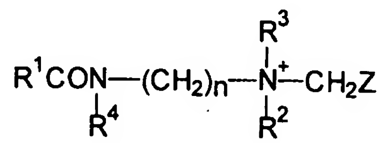
where R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of amphoteric surfactants also include sultaines and amidosultaines. Sultaines, including amidosultaines, include for example, cocodimethylpropylsultaine, stearyldimethylpropylsultaine, lauryl-bis-(2-hydroxyethyl)propylsultaine and the like; and the amidosultaines such as cocamidodimethylpropylsultaine, stearylamidododimethylpropylsultaine, laurylamido-bis-(2-hydroxyethyl)propylsultaine, and the like. Preferred are amidohydroxysultaines such as the C_8-C_{18} hydrocarbylamidopropylhydroxy sultaines, especially C_8-C_{14} hydrocarbylamidopropylhydroxysultaines, *e.g.*,

laurylamidopropylhydroxysultaine and cocamidopropylhydroxysultaine. Other sultaines useful herein are described in U.S. Patent 3,950,417.

Other suitable amphoteric surfactants are the aminoalkanoates of the formula $RNH(CH_2)_nCOOM$, the iminodialkanoates of the formula $RN[(CH_2)_mCOOM]_2$ and mixtures thereof; wherein n and m are numbers from 1 to about 4, R is C_8-C_{22} alkyl or alkenyl, and M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium.

Other suitable amphoteric surfactants include those represented by the formula :



wherein R^1 is C_8-C_{22} alkyl or alkenyl, preferably C_8-C_{16}, R^2 and R^3 is independently selected from the group consisting of hydrogen, $-CH_2CO_2M$, CH_2CH_2OH, $-CH_2CH_2OCH_2CH_2COOM$, or $-(CH_2CH_2O)_mH$ wherein m is an integer from 1 to about 25, and R^4 is hydrogen, $-CH_2CH_2OH$, or $-CH_2CH_2OCH_2CH_2COOM$, Z is CO_2M or CH_2CO_2M, n is 2 or 3, preferably 2, M is hydrogen or a cation, such as alkali metal (*e.g.*, lithium, sodium, potassium), alkaline earth metal (beryllium, magnesium, calcium, strontium, barium), or ammonium. This type of surfactant is sometimes classified as an imidazoline-type amphoteric surfactant, although it should be recognized that it does not necessarily have to be derived, directly or indirectly, through an imidazoline intermediate. Suitable materials of this type are marketed under the tradename MIRANOL and are understood to comprise a complex mixture of species, and can exist in protonated and non-protonated species depending upon pH with respect to species that can have a hydrogen at R^2. All such variations and species are meant to be encompassed by the above formula.

Examples of surfactants of the above formula are monocarboxylates and di-carboxylates. Examples of these materials include cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate (alternately referred to as cocoamphodiacetate), and cocoamphoacetate.

Commercial amphoteric surfactants include those sold under the trade names MIRANOL C2M CONC. N.P., MIRANOL C2M CONC. O.P., MIRANOL C2M SF, MIRANOL CM SPECIAL (Miranol, Inc.); ALKATERIC 2CIB (Alkaril

Chemicals); AMPHOTERGE W-2 (Lonza, Inc.); MONATERIC CDX-38, MONATERIC CSH-32 (Mona Industries); REWOTERIC AM-2C (Rewo Chemical Group); and SCHERCOTERIC MS-2 (Scher Chemicals).

Betaine surfactants, *i.e.* zwitterionic surfactants, suitable for use in the conditioning compositions are those represented by the formula:

$$R^5-[\overset{O}{\overset{\|}{C}}-\overset{R^4}{\overset{|}{N}}-(CH_2)_m]_n-\overset{R^2}{\overset{|}{\underset{\underset{R^3}{|}}{N^+}}}-Y-R^1$$

wherein: R^1 is a member selected from the group consisting of COOM and $CH(OH)CH_2SO_3M$; R^2 is lower alkyl or hydroxyalkyl; R^3 is lower alkyl or hydroxyalkyl; R^4 is a member selected from the group consisting of hydrogen and lower alkyl; R^5 is higher alkyl or alkenyl; Y is lower alkyl, preferably methyl; m is an integer from 2 to 7, preferably from 2 to 3; n is the integer 1 or 0; M is hydrogen or a cation, as previously described, such as an alkali metal, alkaline earth metal, or ammonium. The term "lower alkyl" or "hydroxyalkyl" means straight or branch chained, saturated, aliphatic hydrocarbon radicals and substituted hydrocarbon radicals having from one to about three carbon atoms such as, for example, methyl, ethyl, propyl, isopropyl, hydroxypropyl, hydroxyethyl, and the like. The term "higher alkyl or alkenyl" means straight or branch chained saturated (*i.e.*, "higher alkyl") and unsaturated (*i.e.*, "higher alkenyl") aliphatic hydrocarbon radicals having from about 8 to about 20 carbon atoms such as, for example, lauryl, cetyl, stearyl, oleyl, and the like. It should be understood that the term "higher alkyl or alkenyl" includes mixtures of radicals which may contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such as hydroxyl or halogen radicals wherein the radical remains of hydrophobic character.

Examples of surfactant betaines of the above formula wherein n is zero which are useful herein include the alkylbetaines such as cocodimethylcarboxymethylbetaine, lauryldimethylcarboxymethylbetaine, lauryldimethyl-α-carboxyethylbetaine, cetyldimethylcarboxymethylbetaine, lauryl-bis-(2-hydroxyethyl)-carboxymethylbetaine, stearyl-bis-(2-hydroxypropyl)carboxymethylbetaine, oleyldimethyl-γ-carboxypropylbetaine, lauryl-bis-(2-hydroxypropyl)-α-carboxyethylbetaine, etc. The sulfobetaines may be represented by cocodimethylsulfopropylbetaine,

stearyldimethylsulfopropylbetaine, lauryl-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

Specific examples of amido betaines and amidosulfobetaines useful in the conditioning compositions include the amidocarboxybetaines, such as cocamidodimethylcarboxymethylbetaine, laurylamidodimethylcarboxymethylbetaine, cetylamidodimethylcarboxymethylbetaine, laurylamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, cocamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, etc. The amidosulfobetaines may be represented by cocamidodimethylsulfopropylbetaine, stearylamidodimethylsulfopropylbetaine, laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

3. <u>Highly solubilizing surfactants</u>

In one embodiment, the shampoo compositions of the present invention are preferably free of highly solubilizing surfactants such as N-acyl amino acid surfactants. As used in this context, "substantially free" means that the shampoo compositions preferably contain no more than about 1%, more preferably no more than about 0.5%, more preferably no more than about 0.25%, more preferably essentially zero percent, of highly solubilizing surfactants by weight of the shampoo compositions.

Less preferably, the shampoo compositions may include N-acyl amino acid surfactants as a secondary optional surfactant or as the detersive surfactant component of the shampoo compositions.

N-acyl amino acid surfactants are well known surfactants for use in a variety of products. A description of these surfactants and their synthesis can be found, for example, in <u>Anionic Surfactants, Part II, Surfactant Science Series, Vol. III</u>, edited by Warner M. Linfield, Marcel Dekker, Inc. (New York and Basel), pp. 581-617 (1976).

Suitable N-acyl amino acid surfactants for use in the shampoo compositions herein include N-acyl hydrocarbyl acids and salts thereof, which can be represented by the formula:

$$R^1\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}\overset{\displaystyle R^2}{\overset{|}{N}}\text{—}\left[R^3\right]_n\text{—}COOM$$

wherein R^1 is a alkyl or alkenyl radical having from about 8 to about 24 carbon atoms, preferably from about 12 to about 18 carbons atoms; R^2 is hydrogen, alkyl having from about 1 to about 4 carbon atoms, phenyl, or CH_2COOM,

preferably alkyl having from about 1 to about 4 carbon atoms, more preferably alkyl having from about 1 to about 2 carbon atoms; R^3 is $(CR^4)_2$ or alkoxy having from about 1 or about 2 carbon atoms, wherein each R^4 is independently hydrogen or alkyl having from about 1 to about 6 carbon atoms or alkylester thereof; n is an integer from 1 to 4, preferably 1 or 2; and M a hydrogen, alkali metal (*e.g.*, lithium, sodium, potassium), alkali earth metal (*e.g.*, beryllium, magnesium, calcium, strontium, barium) ammonium or substituted ammonium. Especially preferred are N-acyl sarcosinates and acids thereof, examples of which include lauroyl sarcosinate, myristoyl sarcosinate, cocoyl sarcosinate, and oleoyl sarcosinate, preferably as sodium or potassium salts.

It has been found that the highly solubilizing surfactants described hereinabove, when used in combination with the guar cationic polymers described hereinafter, are less effective in providing improved deposition of the antimicrobial agent of the shampoo compositions herein. It has also been found that, by increasing the cationic charge density of the guar cationic polymer in the presence of these highly solubilizing surfactant, the less effective antimicrobial agent deposition can be improved substantially. In the presence of the highly solubilizing surfactants in the shampoo compositions herein, therefore, the cationic guar polymer should have a cationic charge density of from about 0.9meq/g to about 4meq/g, preferably between about 1.0 and 3meq/g.

B. <u>Antimicrobial Agent</u>

The shampoo compositions of the present invention include a safe and effective amount of an antimicrobial agent. The antimicrobial agent provides the shampoo compositions with antimicrobial activity. The antimicrobial agent is preferably a crystalline particulate that is insoluble in, and dispersed throughout, the shampoo compositions. Effective concentrations of such antimicrobial agents generally range from about 0.1% to about 5%, more preferably from about 0.3% to about 5%, by weight of the shampoo compositions. Suitable antimicrobial agents include sulfur, octopirox, selenium sulfide, and pyridinethione salts.

Without being bound by theory, it is believed this anti-microbial activity results in the reduction of dandruff experienced by the user. In previously known anti-dandruff compositions, relatively large particles of antimicrobial agent are easier to deposit on the scalp than smaller sized particles. However, it is believed improved anti-microbial activity (and consequently improved anti-

dandruff control) can be achieved by reducing the average particle diameter of the antimicrobial agent, thereby increasing the surface area of the antimicrobial agent. The cationic guar polymer component of the present invention facilitates deposition of these relatively small sized particles to the scalp. Generally, the anti-microbial agent may have an average particle size of up to about 20μm, more preferably up to about 15μm, more preferably up to about 10μm, more preferably up to about 8μm, more preferably up to about 5μm, more preferably up to about 3μm; as measured by forward laser light scattering device, *e.g.*, Malvern 3600 instrument. In a preferred embodiment, the average particle size is from about 0.5μm to about 3μm, more preferably about 2.5μm.

Selenium sulfide is a preferred particulate antimicrobial agent for use in the shampoo compositions, effective concentrations of which range from about 0.1% to about 5%, preferably from about 0.3% to about 2.5%, more preferably from about 0.5% to about 1.5%, by weight of the shampoo compositions. Selenium sulfide is generally regarded as a compound having one mole of selenium and two moles of sulfur, although it may also be a cyclic structure, Se_xS_y, wherein x + y = 8. Selenium sulfide compounds are well known in the shampoo art, and are described, for example in U.S. Patent 2,694,668; U.S. Patent 3,152,046; U.S. Patent 4,089,945; and U.S. Patent 4,885,107.

Pyridinethione antimicrobial agents, especially 1-hydroxy-2-pyridinethione salts, are highly preferred particulate antimicrobial agents for use in the shampoo compositions, concentrations of which range from about 0.1% to about 3%, preferably about 0.3% to about 2%, by weight of the shampoo compositions. Preferred pyridinethione salts are those formed from heavy metals such as zinc, tin, cadmium, magnesium, aluminum and zirconium. Zinc salts are most preferred, especially the zinc salt of 1-hydroxy-2-pyridinethione (zinc pyridinethione, ZPT). Other cations such as sodium may also be suitable. Particularly preferred are 1-hydroxy-2-pyridinethione salts in platelet particle form.

Pyridinethione antimicrobial agents are well known in the shampoo art, and are described, for example, in U.S. Patent 2,809,971; U.S. Patent 3,236,733; U.S. Patent 3,753,196; U.S. Patent 3,761,418; U.S. Patent 4,345,080; U.S. Patent 4,323,683; U.S. Patent 4,379,753; and U.S. Patent 4,470,982.

Sulfur may also be used as the particulate antimicrobial agent in the shampoo compositions herein. Effective concentrations of the particulate sulfur are generally from about 1% to about 5%, more preferably from about 2% to about 5%, by weight of the compositions.

Octopirox and related salts and derivatives may also be used as the antimicrobial agent in the shampoo compositions. Such antimicrobial agents are soluble in the shampoo composition and, therefore, do not disperse throughout the composition as crystalline particulates as do the other antimicrobial agents described hereinbefore.

C. Suspending or Thickening Agent

The shampoo compositions of the present invention include a suspending or thickening agent to help maintain dispersion of particulate antimicrobial agents throughout the composition. Any known suspending or thickening agent may be used in the shampoo compositions, provided that it is physically and chemically compatible with the essential components of the shampoo composition described herein, or does not otherwise unduly impair product stability, aesthetics or performance.

Crystalline suspending agents are preferred for suspending the particulate antimicrobial agent in the shampoo compositions. The selected suspending agent, at the selected concentration, should help maintain the suspension for at a period of at least one month, preferably at least three months, more preferably at least about twenty-four months, at ambient temperatures. In general, effective concentrations of the crystalline suspending agent range from about 0.5% to about 10%, preferably from about 0.5% to about 5%, more preferably about 1% to about 4%, more preferably about 1% to about 3%, by weight of the shampoo composition.

In general, concentrations of the crystalline suspending agent should be minimized to achieve only the desired property.

Preferred crystalline suspending agents are acyl derivatives and amine oxides, especially acyl derivatives, especially those which can be solubilized in a premix solution and then be recrystallized upon cooling. These materials include long chain (*e.g.*, C_8-C_{22} preferably C_{14}-C_{22}, more preferably C_{16}-C_{22}) aliphatic groups, *i.e.*, long chain acyl derivative materials and long chain amine oxides, as well as mixtures of such materials. Included are ethylene glycol long chain esters, alkanol amides of long chain fatty acids, long chain esters of long chain

fatty acids, glyceryl long chain esters, long chain esters of long chain alkanolamides, and long chain alkyl dimethyl amine oxides, and combinations thereof.

Crystalline suspending agents are described, for example, in U.S. Patent 4,741,855.

Suitable suspending agents for use in the shampoo compositions herein include ethylene glycol esters of fatty acids preferably having from about 14 to about 22 carbon atoms, more preferably from about 16 to about 22 carbon atoms. More preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms. Preferred alkanol amides are stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain fatty acids (*e.g.*, stearyl stearate, cetyl palmitate); glyceryl esters (*e.g.*, glyceryl distearate) and long chain esters of long chain alkanol amides (*e.g.*, stearamide diethanolamide distearate, stearamide monoethanolamide stearate). Ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids, in addition to the preferred materials listed above, may be used as suspending agents.

Suspending agents also include long chain amine oxides such as alkyl (C_{16}-C_{22}) dimethyl amine oxides, *e.g.*, stearyl dimethyl amine oxide.

Other long chain acyl derivatives that can be used include N,N-dihydrocarbyl (C_{12}-C_{22}, preferably C_{16}-C_{18}) amido benzoic acid and soluble salts thereof (*e.g.*, Na and K salts), particularly N,N-di (C_{16}-C_{18}, and hydrogenated tallow) amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

The crystalline suspending agent can be incorporated into the shampoo compositions herein by solubilizing it into a solution containing water and the anionic sulfate surfactant at a temperature above the melting point of the suspending agent. The suspending agent is then recrystallized, typically by cooling the solution to a temperature sufficient to induce crystallization.

Other suitable suspending agents for use in the shampoo compositions include that can be used include polymeric thickeners, such as carboxyvinyl polymers, examples of which are described in U.S. Patent 2,798,053, and U.S. Patent 4,686,254. Examples of suitable carboxyvinyl polymers include Carbopol® 934, -940, -941, -956, -980, -981, -1342, and -1382, all commercially available from B. F. Goodrich Company

Other suitable suspending agents include those which impart a gel-like viscosity to the composition, such as water soluble or colloidally water soluble polymers like cellulose ethers (*e.g.*, hydroxyethyl cellulose), guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other thickeners, viscosity modifiers, gelling agents, xanthan gum and combinations thereof.

Other suitable suspending agents are described in U.S. Patent 4,788,006.

D. Cationic Guar Polymer

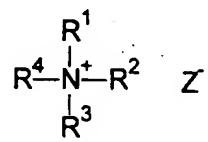
The shampoo compositions of the present invention include a cationic guar polymer having a select charge density. The cationic guar polymer, in combination with the essential components of the compositions, provides improved deposition of the antimicrobial agent onto the scalp and other areas of the skin.. Concentrations of the cationic deposition polymer range from about 0.01% to about 1%, preferably from about 0.01% to about 0.5%, more preferably from about 0.02% to about 0.25%, by weight of the shampoo compositions.

The cationic guar polymer for use in the shampoo composition is further defined as having a cationic charge density of from about 0.01meq/g to about 3meq/g, preferably from about 0.1meq/g to about 2meq/g, more preferably from about 0.8 to about 1.8meq/g, wherein at least about 50%, preferably about 100%, by weight of the cationic guar polymer forms coacervates with detersive surfactant in the shampoo compositions. The formed coacervates are in the form of hydrated, dispersed colloids that are insoluble in the shampoo compositions.

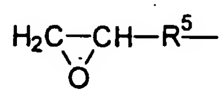
The cationic guar polymers for use in the shampoo compositions are cationically substituted galactomannan (guar) gum derivatives. The molecular weight of such derivatives ranges generally from about 2,000 to about 3,000,000, preferably from about 810,000 to about 3,000,000, more preferably from about 1,000,000 to about 2,500,000. Guar gum for use in preparing these guar gum derivatives is typically obtained as a naturally occurring material from

the seeds of the guar plant. The guar molecule itself is a straight chain mannan branched at regular intervals with single membered galactose units on alternative mannose units. The mannose units are linked to each other by means of beta (1-4) glycosidic linkages. The galactose branching arises by way of an alpha (1-6) linkage. Cationic derivatives of the guar gums are obtained by reaction between the hydroxyl groups of the polygalactomannan and reactive quaternary ammonium compounds. The degree of substitution of the cationic groups onto the guar structure must be sufficient to provide the requisite cationic charge density described hereinbefore.

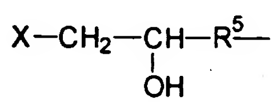
Suitable quaternary ammonium compounds for use in forming the guar cationic polymers include



wherein where R^1, R^2 and R^3 are methyl or ethyl groups and R^4 is an epoxyalkyl group of the formula

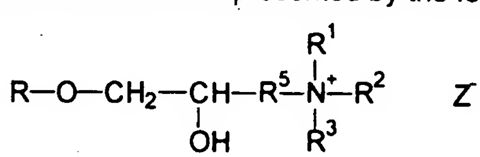


or R^4 is a halohydrin group of the formula



where R^5 is C_1-C_3 alkylene and X is chlorine or bromine, and Z is an anion such as Cl^-, Br^-, I^-, or HSO_4^-.

Cationic guar polymers (cationic derivatives of guar gum) formed from the reagents described hereinbefore are represented by the formula



wherein R is guar gum. Preferably, the cationic guar polymer is guar hydroxypropyltrimethylammonium chloride, which can be more specifically represented by the formula

$$R{-}O{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2N^{+}(CH_3)_3CL^{-}$$

specific examples of which include JAGUAR™ C-13-S (cationic charge density 0.8meq/g) and Jaguar C-17 (cationic charge density 1.6meq/g) commercially available from Rhone-Poulenc Surfactants and Specialties, Cranbury N..J. U.S.A. Other suitable cationic guar polymers include hydroxypropylated cationic guar derivatives.

E. <u>Cool-Feeling Agent</u>

The shampoo compositions of the present invention include a safe and effective amount of a cool-feeling agent sufficient to impart a refreshing and/or cool feeling to the scalp during and/or after shampooing. Preferably, such a cool-feeling effect is a physiological effect due to the direct action of the cool-feeling agent on the nerve endings of the user's body, responsive to the detection of hot or cold, and is not due to latent heat evaporation. Without being bound by theory, it is believed such preferred cool-feeling agents (*e.g.*, menthol) act as a direct stimulus on the cold receptors at the nerve endings, which in turn stimulate the central nervous system.

Concentrations of the cool-feeling agent preferably range from about 0.01% to about 5% of the cool-feeling agent, more preferably from about 0.1% to about 1.5%, more preferably from about 0.3% to about 0.6%, by weight of the shampoo compositions.

Preferably, the cool-feeling agent is selected from the group consisting of borneol, camphor, carboxamides, cineol menthone, glycosil-mono-menthyl-O-acetate, menthol, 3-1-menthoxypropane-1-2-diol, menthyl malonate, 1-menthyl-3-hydroxybutyrate, menthyl salicylate, peppermint, spearmint, and mixtures thereof.

Preferred carboxamides include N-substituted-p-methane-3-carboximides as set forth in U.S. Patent 4,136,163 (Wason *et al.*; issued Jan. 23, 1979); and the acyclic tertiary and secondary carboxamides set forth in U.S. Patent 4,230,688 (Rawsell *et al.*; issued Oct. 28, 1988).

In one embodiment, the cool-feeling agent is a ketal in combination with a secondary coolant, as described in U.S. Patent 5,451,404 (Furman *et al.*; issued Sep. 19, 1995).

F. Water

The shampoo compositions of the present invention are aqueous systems which include from about 40% to about 92%, preferably from about 50% to about 85%, more preferably from about 60% to about 80%, water by weight of the compositions.

The pH of the shampoo compositions ranges, in general, from about 2 to about 10, preferably from about 3 to about 9, more preferably from about 4 to about 8, more preferably from about 5.5 to about 7.5. For zwitterionic or amphoteric surfactant systems, the pH should be adjusted according to the isoelectric point of the selected surfactant to maintain an anionic species on the selected surfactant prior to forming a coacervate with the cationic guar polymer described herein.

G. Nonionic Surfactant

In one aspect of the present invention, the composition may further contain a nonionic surfactant. The level and species of the additional nonionic surfactant are selected according to the compatibility with other components, and desired characteristic of the product.

Nonionic surfactants useful herein include those compounds produced by condensation of alkylene oxide groups, hydrophilic in nature, with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

Preferred nonlimiting examples of nonionic surfactants for use in the shampoo compositions include the following:

(1) polyethylene oxide condensates of alkyl phenols, *e.g.*, the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol;

(2) those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products;

(3) condensation products of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configurations, with ethylene oxide, *e.g.*, a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms;

(4) long chain tertiary amine oxides of the formula [$R^1R^2R^3N \rightarrow O$] where R^1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R^2 and R^3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, *e.g.*, methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals;

(5) long chain tertiary phosphine oxides of the formula [$RR'R''P \rightarrow O$] where R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties and R' and R" are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms;

(6) long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties;

(7) alkyl polysaccharide (APS) surfactants (*e.g.* alkyl polyglycosides), examples of which are described in U.S. Patent 4,565,647, which discloses APS surfactants having a hydrophobic group with about 6 to about 30 carbon atoms and a polysaccharide (*e.g.*, polyglycoside) as the hydrophilic group; optionally, there can be a polyalkylene-oxide group joining the hydrophobic and hydrophilic moieties; and the alkyl group (*i.e.*, the hydrophobic moiety) can be saturated or unsaturated, branched or unbranched, and unsubstituted or substituted (*e.g.*, with hydroxy or cyclic rings); a preferred material is alkyl polyglucoside which is commercially available from Henkel, ICI Americas, and Seppic; and

(8) polyoxyethylene alkyl ethers such as those of the formula $RO(CH_2CH_2)_nH$ and polyethylene glycol (PEG) glyceryl fatty esters, such as those of the formula $R(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$, wherein n is from 1 to about 200, preferably from about 20 to about 100, and R is an alkyl having from about 8 to about 22 carbon atoms.

H. <u>Additional Conditioning Agent</u>

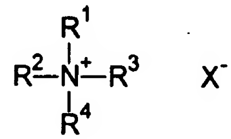
In another aspect of the present invention, the composition may further comprise from about 0.05% to about 20%, preferably from about 0.1% to about 10%, and more preferably from about 0.5% to about 10% of additional conditioning agents selected from the group consisting of cationic surfactants,

silicone compounds, high melting point compounds, oily compounds, nonionic polymers, polyalkylene glycols, and mixtures thereof.

1. Cationic surfactant

The cationic surfactants useful herein are any known to the artisan.

Among the cationic surfactants useful herein are those corresponding to the general formula (I):



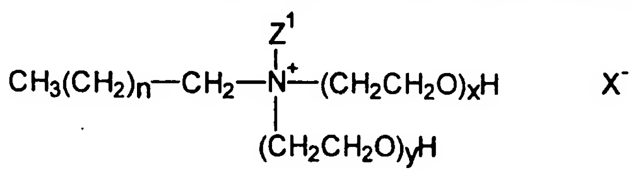
(I)

wherein at least one of R^1, R^2, R^3 and R^4 is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of R^1, R^2, R^3 and R^4 are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (*e.g.* chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, *e.g.*, those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R^1, R^2, R^3 and R^4 are independently selected from C_1 to about C_{22} alkyl. Nonlimiting examples of cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-8, quaternium-14, quaternium-18, quaternium-18 methosulfate, quaternium-24, and mixtures thereof.

Among the cationic surfactants of general formula (I), preferred are those containing in the molecule at least one alkyl chain having at least 16 carbons. Nonlimiting examples of such preferred cationic surfactants include: behenyl trimethyl ammonium chloride available, for example, with tradename INCROQUAT TMC-80 from Croda and ECONOL TM22 from Sanyo Kasei; cetyl trimethyl ammonium chloride available, for example, with tradename CA-2350 from Nikko Chemicals, hydrogenated tallow alkyl trimethyl ammonium chloride, dialkyl (14-18) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride, dihydrogenated tallow alkyl dimethyl ammonium chloride, distearyl

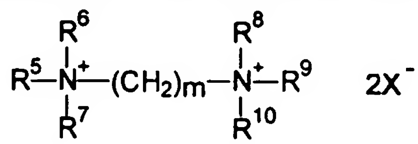
dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, di(behenyl/arachidyl) dimethyl ammonium chloride, dibehenyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl propyleneglycol phosphate dimethyl ammonium chloride, stearoyl amidopropyl dimethyl benzyl ammonium chloride, stearoyl amidopropyl dimethyl (myristylacetate) ammonium chloride, and N-(stearoyl colamino formyl methy) pyridinium chloride.

Also preferred are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R^1-R^4 radicals contain one or more hydrophilic moieties selected from alkoxy (preferably C_1-C_3 alkoxy), polyoxyalkylene (preferably C_1-C_3 polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically substituted cationic surfactants include those of the formula (II) through (VIII) below:



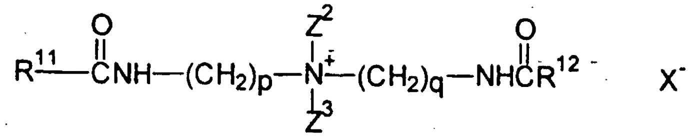
(II)

wherein n is from 8 to about 28, x+y is from 2 to about 40, Z^1 is a short chain alkyl, preferably a C^1-C^3 alkyl, more preferably methyl, or $(CH_2CH_2O)_zH$ wherein x+y+z is up to 60, and X is a salt forming anion as defined above;

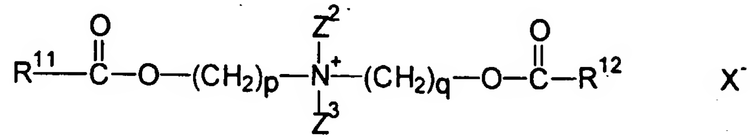


(III)

wherein m is 1 to 5, one or more of R^5, R^6, and R^7 are independently an C_1-C_{30} alkyl, the remainder are CH_2CH_2OH, one or two of R^8, R^9, and R^{10} are independently an C_1-C_{30} alkyl, and remainder are CH_2CH_2OH, and X is a salt forming anion as mentioned above;

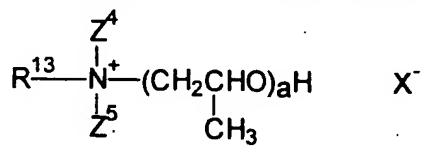


(IV)



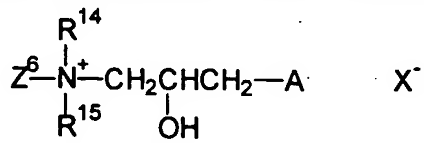
(V)

wherein, independently for formulae (IV) and (V), Z^2 is an alkyl, preferably C_1-C_3 alkyl, more preferably methyl, and Z^3 is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl, p and q independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2, R^{11} and R^{12}, independently, are substituted or unsubstituted hydrocarbyls, C_{12}-C_{20} alkyl or alkenyl, and X is a salt forming anion as defined above;



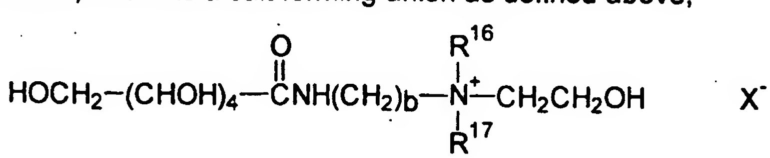
(VI)

wherein R^{13} is a hydrocarbyl, preferably a C_1-C_3 alkyl, more preferably methyl, Z^4 and Z^5 are, independently, short chain hydrocarbyls, preferably C_2-C_4 alkyl or alkenyl, more preferably ethyl, a is from 2 to about 40, preferably from about 7 to about 30, and X is a salt forming anion as defined above;



(VII)

wherein R^{14} and R^{15}, independently, are C_1-C_3 alkyl, preferably methyl, Z^6 is a C12-C22 hydrocarbyl, alkyl carboxy or alkylamido, and A is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and X is a salt forming anion as defined above;



(VIII)

wherein b is 2 or 3, R^{16} and R^{17}, independently are C_1-C_3 hydrocarbyls preferably methyl, and X is a salt forming anion as defined above. Nonlimiting examples of hydrophilically substituted cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-16, quaternium-26, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-61, quaternium-62, quaternium-70, quaternium-71, quaternium-72, quaternium-75, quaternium-76 hydrolyzed collagen, quaternium-77, quaternium-78, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79 hydrolyzed silk, quaternium-79 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein, quaternium-80, quaternium-81, quaternium-82, quaternium-83, quaternium-84, and mixtures thereof.

Highly preferred hydrophilically substituted cationic surfactants include dialkylamido ethyl hydroxyethylmonium salt, dialkylamidoethyl dimonium salt, dialkyloyl ethyl hydroxyethylmonium salt, dialkyloyl ethyldimonium salt, and mixtures thereof; for example, commercially available under the following tradenames; VARISOFT 110, VARIQUAT K1215 and 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265 from ICI Americas.

Salts of primary, secondary, and tertiary fatty amines are also suitable cationic surfactants. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and can be substituted or unsubstituted. Particularly useful are amido substituted tertiary fatty amines. Such amines, useful herein, include stearamidopropyldimethylamine, stearamidopropyldiethylamine, stearamidoethyldiethylamine, stearamidoethyldimethylamine, palmitamidopropyldimethylamine, palmitamidopropyldiethylamine, palmitamidoethyldiethylamine, palmitamidoethyldimethylamine, behenamidopropyldimethylamine, behenamidopropyldiethylamine, behenamidoethyldiethylamine, behenamidoethyldimethylamine, arachidamidopropyldimethylamine, arachidamidopropyldiethylamine, arachidamidoethyldiethylamine,

arachidamidoethyldimethylamine, diethylaminoethylstearamide. Also useful are dimethylstearamine, dimethylsoyamine, soyamine, myristylamine, tridecylamine, ethylstearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide) stearylamine, dihydroxyethylstearylamine, and arachidylbehenylamine. These amines can also be used in combination with acids such as L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, tartaric acid, citric acid, L-glutamic hydrochloride, and mixtures thereof; more preferably L-glutamic acid, lactic acid, citric acid. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, *et al.*.

The cationic surfactants for use herein may also include a plurality of ammonium quaternary moieties or amino moieties, or a mixture thereof.

2. Silicone compounds

The present invention comprises by weight from about 0.01% to about 20%, preferably from about 0.05% to about 10% of a silicone compound. The silicone compounds useful herein include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone. The silicone compounds herein may be made by any suitable method known in the art, including emulsion polymerization. The silicone compounds may further be incorporated in the present composition in the form of an emulsion, wherein the emulsion is made my mechanical mixing, or in the stage of synthesis through emulsion polymerization, with or without the aid of a surfactant selected from anionic surfactants, nonionic surfactants, cationic surfactants, and mixtures thereof.

The silicone compounds for use herein will preferably have a viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000, and even more preferably from about 100,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970. Silicone compound of high molecular weight may be made by emulsion polymerization. Suitable silicone fluids include polyalkyl

siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicone compounds having hair conditioning properties can also be used.

The silicone compounds herein also include polyalkyl or polyaryl siloxanes with the following structure (I)

$$A-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{Si}}}}-O\left[\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{Si}}}}-O\right]_x-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{Si}}}}-A \qquad \text{(I)}$$

wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

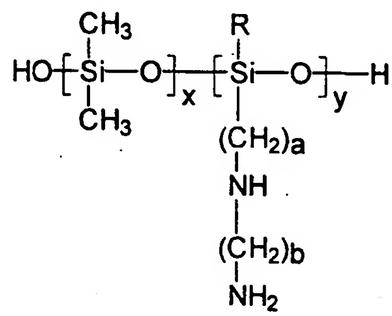
Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as

described below to decrease the surface tension and enhance the film forming ability of the material.

The silicone compounds that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Other silicone compounds include amino substituted materials. Suitable alkylamino substituted silicone compounds include those represented by the following structure (II)



(II)

wherein R is CH_3 or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino substituted silicone fluids include those represented by the formula (III)

$$(R^1)_aG_{3-a}\text{—Si—}(OSiG_2)_n\text{—}(OSiG_b(R^1)_{2-b})_m\text{—O—}SiG_{3-a}(R^1)_a \qquad \text{(III)}$$

in which G is chosen from the group consisting of hydrogen, phenyl, OH, C_1-C_8 alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R^1 is a monovalent radical of formula C_qH2_qL in which q is an integer from 2 to 8 and L is chosen from the groups

—$N(R^2)CH_2$—CH_2—$N(R^2)_2$

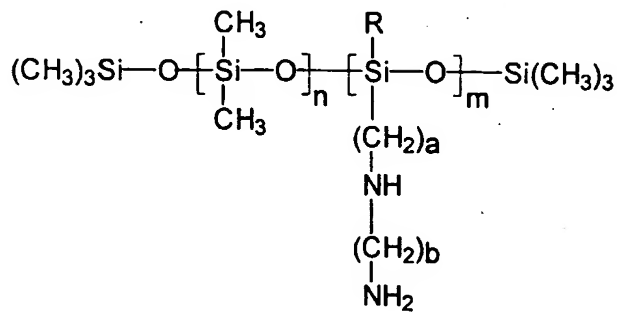
—$N(R^2)_2$

—$N(R^2)_3A^-$

$$—N(R^2)CH_2—CH_2—NR^2H_2A^-$$

in which R^2 is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A^- denotes a halide ion.

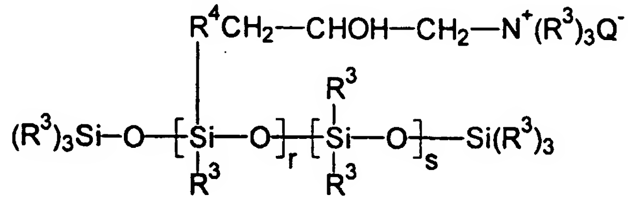
An especially preferred amino substituted silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



(IV)

In this formula n and m are selected depending on the exact molecular weight of the compound desired.

Other amino substituted silicone polymers which can be used are represented by the formula (V):



(V)

where R^3 denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R_4 denotes a hydrocarbon radical, preferably a C_1-C_{18} alkylene radical or a C_1-C_{18}, and more preferably C_1-C_8, alkyleneoxy radical; Q^- is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

References disclosing suitable nonvolatile dispersed silicone compounds include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British

Patent No. 849,433, to Woolston. "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984, provides an extensive, though not exclusive, listing of suitable silicone compounds.

Another nonvolatile dispersed silicone that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer *et al.*, issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General

Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospearl™ from Toshiba Silicones.

The method of manufacturing these silicone compounds, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp. 204-308, John Wiley & Sons, Inc..

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit $(CH_3)_3SiO)_{.5}$; D denotes the difunctional unit $(CH_3)_2SiO$; T denotes the trifunctional unit $(CH_3)SiO_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2. Primes of the unit symbols, *e.g.*, M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to

about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

Commercially available silicone compounds which are useful herein include Dimethicone with tradename D-130, cetyl Dimethicone with tradename DC2502, stearyl Dimethicone with tradename DC2503, emulsified polydimethyl siloxanes with tradenames DC1664 and DC1784, and alkyl grafted copolymer silicone emulsion with tradename DC2-2845; all available from Dow Corning Corporation, and emulsion polymerized Dimethiconol available from Toshiba Silicone as described in GB application 2,303,857.

3. <u>High melting point compound</u>

The compositions may comprise a high melting point compound having a melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of combing. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, *e.g.*, some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more

preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; ceteareth 1 through ceteareth-10, which are the ethylene glycol ethers of ceteareth alcohol, *i.e.* a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C_1-C_{30} alkyl ethers of the ceteth, steareth, and ceteareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By

"pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from New Japan Chemical (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

4. Oily compound

Oily compounds useful herein preferably have a melting point of not more than about 25°C selected, and are selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof. The oily compounds useful herein may be volatile or nonvolatile. Without being bound by theory, it is believed that, the oily compounds may penetrate the hair to modify the hydroxy bonds of the hair, thereby resulting in providing softness and flexibility to the hair. The oily compound may comprise either the first oily compound or the second oily compound as described herein. Preferably, a mixture of the first oily compound and the second oily compound is used. The oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the oily compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

a. First oily compound

The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl

alchol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol and lauryl alcohol.

The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, Oleth-2, pentaerythritol tetraoleate, pentaerythritol tetraisostearate, trimethylolpropane trioleate, and trimethylolpropane triisostearate.

Commercially available first oily compounds useful herein include: oleyl alcohol with tradename UNJECOL 90BHR available from New Japan Chemical, pentaerythritol tetraisostearate and trimethylolpropane triisostearate with tradenames KAKPTI and KAKTTI available from Kokyu Alcohol (Chiba, Japan), pentaerythritol tetraoleate having the same tradename as the compound name available from New Japan Chemical, trimethylolpropane trioleate with a tradename ENUJERUBU available from New Japan Chemical, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isoproplyl isostearate having a tradename ZPIS available from Kokyu Alcohol.

b. <u>Second oily compound</u>

The second oily compounds useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22

carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C_{2-6} alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have substantially higher chain lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available second oily compounds useful herein include isododecane, isohexadeance, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South Plainfield New Jersey, USA), a copolymer of isobutene and normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco, isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA), α-olefin oligomer with tradename PURESYN 6 from Mobil Chemical Co., and trimethylolpropane tricaprylate/tricaprate with tradename MOBIL ESTER P43 from Mobil Chemical Co.

5. Nonionic polymer

Nonionic polymers useful herein include cellulose derivatives, hydrophobically modified cellulose derivatives, ethylene oxide polymers, and ethylene oxide/propylene oxide based polymers. Suitable nonionic polymers are cellulose derivatives including methylcellulose with tradename BENECEL, hydroxyethyl cellulose with tradename NATROSOL, hydroxypropyl cellulose with tradename KLUCEL, cetyl hydroxyethyl cellulose with tradename POLYSURF 67, all supplied by Herculus. Other suitable nonionic polymers are ethylene oxide and/or propylene oxide based polymers with tradenames CARBOWAX PEGs, POLYOX WASRs, and UCON FLUIDS, all supplied by Amerchol.

6. Polyalkylene glycols

These compounds are particularly useful for compositions which are designed to impart a soft, moist feeling to the hair. When present, the polyalkylene glycol is typically used at a level from about 0.025% to about 1.5%, preferably from about 0.05% to about 1%, and more preferably from about 0.1% to about 0.5% of the compositions.

The polyalkylene glycols are characterized by the general formula:

$$H(OCH_2\underset{\substack{|\\R}}{C}H)_n\text{—}OH$$

wherein R is selected from the group consisting of H, methyl, and mixtures thereof. When R is H, these materials are polymers of ethylene oxide, which are also known as polyethylene oxides, polyoxyethylenes, and polyethylene glycols. When R is methyl, these materials are polymers of propylene oxide, which are also known as polypropylene oxides, polyoxypropylenes, and polypropylene glycols. When R is methyl, it is also understood that various positional isomers of the resulting polymers can exist.

In the above structure, n has an average value of from about 1500 to about 25,000, preferably from about 2500 to about 20,000, and more preferably from about 3500 to about 15,000.

Polyethylene glycol polymers useful herein are PEG-2M wherein R equals H and n has an average value of about 2,000 (PEG-2M is also known as Polyox WSR® N-10, which is available from Union Carbide and as PEG-2,000); PEG-5M wherein R equals H and n has an average value of about 5,000 (PEG-5M is also known as Polyox WSR® N-35 and Polyox WSR® N-80, both available from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M wherein R equals H and n has an average value of about 7,000 (PEG-7M is also known as Polyox WSR® N-750 available from Union Carbide); PEG-9M wherein R equals H and n has an average value of about 9,000 (PEG 9-M is also known as Polyox WSR® N-3333 available from Union Carbide); and PEG-14 M wherein R equals H and n has an average value of about 14,000 (PEG-14M is also known as Polyox WSR® N-3000 available from Union Carbide).

Other useful polymers include the polypropylene glycols and mixed polyethylene/polypropylene glycols.

I. Additional Components

The shampoo compositions of the present invention may include a variety of additional components, which may be selected by the artisan according to the desired characteristics of the final product. Additional components include, for example, polyvalent metal cations, and other additional components.

1. Polyvalent metal cations

Suitable polyvalent metal cations include divalent and trivalent metals, divalent metals being preferred. Exemplary metal cations include alkaline earth metals, such as magnesium, calcium, zinc, and copper, and trivalent metals such as aluminum and iron. Preferred are calcium and magnesium.

The polyvalent metal cation can be added as an inorganic salt, organic salt, or as a hydroxide. The polyvalent metal cation may also be added as a salt with anionic surfactants as mentioned above.

Preferably, the polyvalent metal cation is introduced as an inorganic salt or organic salt. Inorganic salts include chloride, bromide, iodine, nitrate, or sulfate, more preferably chloride or sulfate. Organic salts include L-glutamate, lactate, malate, succinate, acetate, fumarate, L-glutamic acid hydrochloride, and tartarate.

It will be clear to those skilled in the art that, if polyvalent salts of the anionic surfactant is used as the mode of introducing the polyvalent metal cations into the compositions hereof, only a fraction of the anionic surfactant may be of polyvalent form, the remainder of the anionic surfactant being necessarily added in monovalent form.

2. Other additional components

A wide variety of other additional ingredients can be formulated into the present compositions. These include: other conditioning agents such as hydrolyzed collagen with tradename Peptein 2000 available from Hormel, vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; emulsifying surfactants for dispersing water insoluble components in the carrier; hair-fixative polymers such as amphoteric fixative polymers, cationic fixative polymers, anionic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers; optical brighteners such as polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, and imidazoles;

preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate. Such optional ingredients generally are used individually at levels from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0% by weight of the composition.

J. <u>Examples</u>

The following examples further describe and demonstrate the preferred embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration, and are not to be construed as limitations of the present invention since many variations thereof are possible without departing from its spirit and scope. Ingredients are identified by chemical or CTFA (Cosmetic, Toiletry and Fragrance Association) name, or otherwise defined below.

The shampoo compositions of the present invention can be prepared by using conventional mixing and formulating techniques. The shampoo compositions illustrated in Example 1-10 are prepared in the following manner. All percentages are based on weight of total composition unless otherwise specified.

For those examples which include a silicone component, a silicone premix is prepared having the following components by weight of the premix: at least about 50% dimethicone from 5% to about 15% ammonium laureth sulfate, and the remainder water. It should be noted that the ammonium laureth sulfate is added in this premix in the main body of the composition, and after heat processing. The premix is formed by high sheer mixing until the desired silicone particle size is achieved.

For each of the composition illustrated in the example 1-10, from 30% to 100% of the detersive surfactants are added to a jacketed mix tank and heated to about 74°C with slow agitation to form a surfactant solution. Salts (sodium chloride, sodium sulfate) and pH modifiers (disodium phosphate, monosodium

phosphate) are added to the tank and allowed to disperse. Ethylene glycol distearate (EGDS) is added to the mixing vessel and allowed to melt. After the EGDS is melted and dispersed (e.g., after 5 to 20 minutes), preservative and additional viscosity modifier (if necessary) are added to the surfactant solution. The resulting mixture is passed through a heat exchanger where it is cooled to about 35°C and collected in a finishing tank. As a result of this cooling step, the EGDS crystallizes to form a crystalline network in the product. Any remaining surfactants, the silicone premix (for those examples including silicone), and other components are added to the finishing tank with agitation to ensure a homogenous mixture. Cationic guar polymer is dispersed in water as a 0.5 to 2.5% aqueous solution before addition to the final mix. It should be noted that the cool-feeling agent can be added to the finishing tank directly or can be premixed with organic solvent before addition to finishing tank. Once all components have been added, viscosity and pH modifiers are added to the mixture to adjust product viscosity and pH to the extent desired.

Each exemplified composition provides hair cleansing, antimicrobial agent deposition and dandruff control, while providing a cool-feeling sensation to the scalp.

COMPONENT	EXAMPLE NO.				
	1	2	3	4	5
Ammonium Laureth Sulfate	15	13.5	7.5	15	15
Ammonium Lauryl Sulfate	5	4.5	2.5	5	5
Sodium Lauryl Sarcosinate	1.5	1.5	1.5	0.75	----
Cocamidopropyl Betaine	----	----	----	----	2.0
Ethylene Glycol Distearate	1.5	1.5	1.5	1.5	1.5
Zinc Pyrithione	1.0	1.0	1.0	----	1.0
Selenium Disulfide	----	----	----	1.0	----
Jaguar C17	0.1	0.1	0.15	----	----
Jaguar C13S	----	----	----	0.1	0.2
Menthol	3.0	0.5	----	----	0.01
Peppermint	----	----	1.0	----	----
Spearmint	----	----	----	1.0	----
Dimethicone(40% gum/60% fluid)	1.0	1.0	1.0	----	1.0
Laury alcohol	0.15	0.15	0.15	0.15	----
Cetyl Alcohol	0.42	0.42	0.42	----	0.42
Stearyl Alcohol	0.18	0.18	0.18	----	0.18
Fragrance	q.s.	q.s.	q.s.	q.s.	q.s.

Color	q.s.	q.s.	q.s.	q.s.	q.s.
PH adhustment (Mono/Di sodium phosphate)	q.s.	q.s.	q.s.	q.s.	q.s.
Viscosity adjustment (Sodium Chloride)	q.s.	q.s.	q.s.	q.s.	q.s.
Preservative(DMDM hydantoin); Water	q.s.	q.s.	q.s.	q.s.	q.s.

COMPONENT	EXAMPLE NO.				
	6	7	8	9	10
Ammonium Laureth Sulfate	15	14	14	15	15
Ammonium Lauryl Sulfate	5	----	----	5	5
Cocamidopropyl Betaine	----	----	2.5	----	----
Cocoamphodiacetate	----	2.5	----	----	----
Cocamide MEA	1.0	1.0	1.0	----	1.0
Sodium Cocoyl Glutamate	----	----	----	1.5	----
Ethylene Glycol Distearate	1.5	1.5	1.5	1.5	1.5
Zinc Pyrithione	1.0	1.0	1.0	1.0	1.0
Jaguar C17	----	0.2	----	0.1	----
Jaguar C13S	0.15	----	0.2	----	0.15
Menthol	0.5	----	----	----	
Camphor	----	1.75	----	----	
1-menthyl-3-hydroxybutylate	----	----	0.55	----	
Menthylmalonate	----	----	----	0.10	
3-1-menthoxypropane-1-2-diol	----	----	----	----	4.0
Cetyl Alcohol	----	0.42	0.42	----	0.42
Stearyl Alcohol	----	0.18	0.18	----	0.18
Fragrance	q.s.	q.s.	q.s.	q.s.	q.s.
Color	q.s.	q.s.	q.s.	q.s.	q.s.
PH adhustment (Mono/Di sodium phosphate)	q.s.	q.s.	q.s.	q.s.	q.s.
Viscosity adjustment (Sodium Chloride)	q.s.	q.s.	q.s.	q.s.	q.s.
Preservative(DMDM hydantoin); Water	q.s.	q.s.	q.s.	q.s.	q.s.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from the scope of the present invention.

WHAT IS CLAIMED IS:

1. A composition comprising:

(a) from about 7% to about 30% by weight of a detersive surfactant selected from the group consisting of anionic surfactants, amphoteric surfactants, and mixtures thereof;

(b) from about 0.1% to about 10% by weight of an antimicrobial agent;

(c) from about 0.5% to about 10% by weight of a suspending agent;

(d) from about 0.01% to about 1.0% by weight of a cationic guar polymer having a charge density of from about 0.01meq/g to about 3meq/gm;

(e) from about 0.01% to about 5% of a cool-feeling agent selected from the group consisting of borneol, camphor, cineol menthane, glycosil-mono-mentyl-oacetate, menthol, 3-1-menthoxypropane-1-2-diol, menthyl malonate, 1-menthyl-3-hydroxybutyrate, menthyl salicylate, peppermint, spearmint, and mixtures thereof; and

(f) from about 40% to about 92% by weight of water;

wherein at least about 50% by weight of the cationic guar polymer is in coacervate form, the coacervate comprising detersive surfactant and cationic guar polymer.

2. The composition of Claim 1, wherein

(a) the antimicrobial agent is a crystalline, particulate antimicrobial agent selected from the group consisting of sulfur, selenium sulfide, pyridinethione salts, and mixtures thereof; and

(b) the suspending agent is a crystalline suspending agent selected from the group consisting of ethylene glycol esters of fatty acids having from about 14 to about 22 carbon atoms, and mixtures thereof.

3. The composition of Claim 2 wherein the antimicrobial agent is a zinc salt of 1-hydroxy-2-pyridinethione.

4. The composition of Claim 2 wherein the composition is substantially free of N-acyl amino acid surfactants.

5. The composition of Claim 4 wherein the detersive surfactant is an anionic surfactant.

6. The composition of Claim 5 wherein the anionic detersive surfactant is selected from the group consisting of alkyl sulfates, alkyl ether sulfates and combinations thereof.

7. The composition of Claim 6 wherein the cationic guar polymer has a cationic charge density of from about 0.1meq/g to about 2meq/g and a molecular weight of from about 1,000,000 to about 2,500,000.

8. The composition of Claim 7 wherein the cationic guar polymer is guar hydroxypropyltrimethylammonium chloride.

9. The composition of Claim 2 wherein the detersive surfactant comprises an N-acyl amino acid surfactant, and the cationic guar polymer has a cationic charge density of from about 0.9meq/g to about 3meq/g.

10. The composition of any of Claims 1-9, further comprising from about 0.05% to about 20% by weight of an additional conditioning agent selected from the group consisting of cationic surfactants, silicone compounds, high melting point compounds, nonionic polymers, oily compounds, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/02731

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 204 320 A (THE PROCTER AND GAMBLE CO.) 9 November 1988 see claims 1-6 ---	1-3,5,6, 8,10
Y	US 5 624 666 A (COFFINDAFFER, T. W. ET AL.) 29 April 1997 see claims 1,7,11,12,16,17 -----	1-3,5,6, 8,10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 November 1998	24/11/1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/02731

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